

Description

Background of the invention

5 Substituted naphthalenes are known fluorescers and used extensively in the manufacture of chemiluminescent lighting devices in combination with oxalates and peroxide generators. Rubrene per se has been commercially available for many years and is generally produced by the reaction of 1,1,3-triphenylpropargyl alcohol and thionyl chloride with subsequent heating of the resultant reaction product in the presence of an amine base. Oftimes, the rubrene is produced in the form of its sulfonate by reaction with fuming sulfuric acid. Yields of
 10 rubrene utilizing the above procedure, however, are relatively low, i.e., 30-50% and not very reproducible.

Other procedures for the production of rubrene are taught in Moureu et al ; C.R. Acad. Sci. (1926), 182, 1440 ; Moureu et al ; Bull. Soc. Chem. (1930), 216, Wittig et al ; Journal fur praktische Chemie N.F. (1942), 160, 242 ; Rigaudy et al ; Tetrahedron (1977), 33, 767. In each of the procedures set forth above, the yields range from 20-50% and oftimes require the isolation and purification of intermediates.

15 Thus, the industry is always searching for new procedures which enable the recovery of naphthalenes in increased yields and without the need for intermediate isolation and purification.

DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENTS

20 The present invention provides a process for the preparation of substituted naphthalenes which comprises 1) reacting a solvent solution of a 1,3-diphenylpropargyl alcohol, in the presence of an acid scavenger, with an alkanesulfonyl halide at a temperature ranging from -30°C to 30°C for from 15 minutes to 3 hours, 2) heating the reaction product resulting from step 1) to a temperature of from 70°C to reflux for from 2 to 8 hours, in an oxygen-free atmosphere, in the absence of light and in the presence of an hindered amine base and 3) recovering the resultant substituted naphthalene.
 25

Step 1) may be conducted utilizing any material which is a solvent for the solid 1,3-diphenylpropargyl alcohol and the alkanesulfonyl halide and has a boiling point above the temperature at which step 1) is conducted. Suitable solvents include methylene chloride, toluene, xylene mixtures and, dimethylformamide. While it is possible to use the same solvent in Step 1) which is to be used in Step 2), such is not preferred, since it
 30 has been found that higher yields of the naphthalene are achieved when two different solvents are used and furthermore, the recovered naphthalene has a greater purity.

The 1,3-diphenylpropargyl alcohol and alkane sulfonyl halide are preferably reacted in equimolar amounts, however, a slight excess of the halide is tolerable. Higher or lower concentrations of either reactant either result in lower yields of the intermediate or do not enhance the reaction in any significant way.

35 The acid scavenger employed may be any material which is known to be useful for this purpose. Suitable scavengers are the amines such as triethylamine, pyridine, 1,8-diazabicyclo[5.4.0] undeca-7-ene. Diisopropylethylamine and, tetramethylethylenediamine may also be used. Sufficient scavenger should be used to take up substantially all of the acid liberated by the reaction since the presence of an acid media interferes with the naphthalene production since the intermediates are acid sensitive.

40 The reaction of step 1) is conducted at a temperature of from -30°C to 30°C, preferably from -10°C to 10°C, with agitation, for from 15 minutes to 5 hours, preferably from 1 to 3 hours.

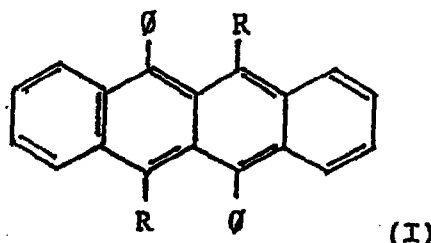
Once the intermediate is formed, step 2) is commenced by first removing the reaction from the light such as by isolating the reaction vessel in the dark or using a light impermeable reaction vessel ab initio. Once light is removed from the reaction media, the media is heated to a temperature ranging from about 70°C to reflux (i.e. depending upon the solvent being employed), preferably from 90°C to 120°C. The heating is continued
 45 for from 2 to 8 hours, preferably from 4 to 6 hours. The reaction media in step 2) is maintained under oxygen-free conditions by feeding nitrogen gas or other equivalent material into the reaction vessel. Sufficient solvent should be retained in the reaction media containing the intermediate to create approximately a 0.5-3.0 M solution. Sufficient amounts of hindered amine base are added, preferably dropwise, to pull off protons from the step 1) intermediate and cause cyclization thereof to the naphthalene structure. Suitable hindered amine bases include
 50 tertiary amines such as pyridine ; substituted pyridines such as 2,4,6-trimethylpyridine ; quinoline ; N,N-dimethylaniline.

When the solvent employed in step 1) is different than that which is to be used in Step 2) it will be necessary to volatilize off said step 1) solvent between step 1) and step 2) and replace said volatilized solvent with a second
 55 solvent. This can be accomplished rather simply by the use of, for example, a Dean-Stark trap. Suitable solvents which may be used in Step 2) include xylenes, toluenes, mixtures thereof and, dimethylformamide.

Recovery of the naphthalene product can be accomplished utilizing any technique known in the art, e.g. filtration, however, purification after recovery is generally conducted, for example, as is shown in U.S. Patent

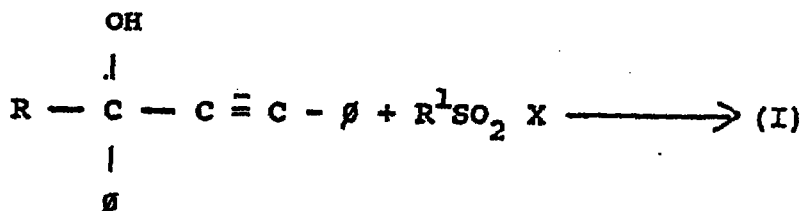
No. 3888784. Generally, recovery is accomplished by filtering the step 2) reaction product through a filter such as a sintered glass funnel using an aspirator. Xylenes or other solvent may be used to remove all solids from the reaction vessel and the crude product may be washed, as required, with methanol until the final filtrate is substantially colorless. The final product naphthacene, is colored, i.e., rubrene per se is orange, and is dried to remove all traces of solvent.

The naphthacene products produced by the process of the present invention have the following structure:



wherein Ø is phenyl and R is hydrogen, phenyl or substituted phenyl, said substituents being alkyl (C₁-C₄), halogen, cyano, nitro, alkoxy (C₁-C₄) groups.

The reaction proceeds according to the equation :



wherein R and Ø are as set forth above, R¹ is alkyl (C₁-C₄) and X is a halide, e.g., chloride, fluoride, iodide.

The following examples are set forth for purposes of illustration of the invention. All parts and percentages are by weight unless otherwise specified.

Example 1

To a suitable reaction vessel equipped with a mechanical stirrer, addition funnel, Dean-Stark trap, condenser, thermometer with adapter, Claisen adapter and nitrogen inlet are charged 533.8 parts of 1,1,3-triphenylpropargyl alcohol and 1060 parts of methylene chloride. The vessel is stirred until all the alcohol is in solution. The solution is pale yellow. The vessel is cooled and 189.8 parts of triethylamine are slowly added while cooling. 215.2 Parts of methanesulfonyl chloride are charged dropwise while maintaining the temperature at 0-5°C. The resultant reaction media is stirred at 0-5°C for one hour and then allowed to warm to room temperature and is then stirred for an additional hour. The reaction vessel is then placed in the dark and the contents heated to drive off the methylene chloride which is collected in the Dean-Stark trap. When 331.2 parts are collected, 215 parts of a commercially available xylene mixture is added. 331.2 More parts of methylene chloride are collected and replaced by 215 parts of said xylene mixture during which the reaction media is about 50°C.

To this reaction media are then added, dropwise, 227.4 parts of 2,4,6-trimethylpyridine while the remaining methylene chloride is collected and replaced by 215 parts of the xylene mixture. The temperature is maintained at 95°C for 6 hours after which the media is cooled to room temperature (30-45 minutes). The resultant reaction media is very thick with solids and is dark red in color. The reaction media is filtered through a sintered glass funnel using an aspirator. Any solids remaining in the reaction vessel are removed by rinsing the vessel several times with xylene. The filtrate is very dark. The crude product is washed nine times with 197.8 part portions of methanol. The final filtrate is colorless. The final product, rubrene, is orange. It is dried overnight to remove traces of methanol. 305 Parts are recovered resulting in a yield of 61%.

Example 2

A reaction vessel equipped with a condenser, mechanical stirrer, thermometer, nitrogen purge, Claisen adapter, addition funnel, and Dean-Stark trap is charged with 10.7 parts of 1,1,3-triphenylpropargyl alcohol and

26.5 parts of methylene chloride. The mixture is stirred until all the solid has dissolved. The solution is pale yellow in color. The reaction vessel is cooled to 0-5°C and then 3.8 parts of triethylamine are slowly added. While maintaining the temperature at 0-5°C, 4.8 parts of ethanesulfonyl chloride are added dropwise. The resultant reaction mixture is stirred at 0-5°C for one hour. The reaction mixture is then warmed to room temperature and stirred for an additional hour at room temperature. The vessel is then protected from light and the contents are heated to distill off the methylene chloride. When 13.2 parts of methylene chloride have been collected, 8.5 parts of a xylene mixture are added along with 4.55 parts of 2,4,6-trimethylpyridine which are added dropwise. When the remaining methylene chloride is collected, 8.7 parts of a xylene mixture are added to the reaction vessel. The temperature is maintained at 100°C for five hours after which it is cooled to room temperature. The resultant reaction mixture is very thick with solids and is dark red in color. The mixture is filtered through a sintered glass funnel using an aspirator. Any solids remaining in the reaction vessel are rinsed out with a xylene mixture. The filtrate is dark red in color. The crude product is washed five times with 15.8 parts of methanol. The final filtrate is colorless. The final product, rubrene, is an orange solid. The purified product is dried under vacuum overnight to remove any traces of methanol. 3.7 Parts of rubrene are recovered resulting in a yield of 37%.

Examples 3-5

Following the procedure of Example 1, except as indicated, various alcohols are reacted with various halides to produce substituted naphthacenes. All substituent designations are as set forth above. The results are set forth in Table I, below.

Table I

Ex. No.	Alcohol	Halide		Naphthacene
	R	R ¹	X	R
3	hydrogen	methane	chloride	hydrogen
4	p-chlorophenyl	methane	bromide	p-chloro-phenyl
5	p-methoxyphenyl	ethane	chloride	p-methoxy-phenyl

Claims

1. A method for the preparation of a naphthacene which comprises 1) reacting a solvent solution of a 1,3-diphenylpropargyl alcohol, in the presence of an acid scavenger, with an alkanesulfonyl halide at a temperature of from -30°C to 30°C for from 15 minutes to 3 hours, 2) heating the resultant reaction product to a temperature of from 70°C to reflux from 2 to 8 hours, in an oxygen-free atmosphere, in the absence of light and in the presence of a hindered amine base and 3) recovering the resultant naphthacene.
2. A method according to Claim 1 wherein said acid scavenger is an amine.
3. A method according to Claim 2 wherein said amine is triethylamine.
4. A method according to Claim 1 wherein said hindered amine base is 2,4,6-trimethylpyridine.
5. A method according to Claim 2 wherein said hindered amine base is 2,4,6-trimethylpyridine.
6. A method according to Claim 1 wherein the said solvent in step 1) is methylene chloride and the solvent in step 2) is a xylene mixture.
7. A method according to Claim 6 wherein said acid scavenger is an amine.
8. A method according to Claim 7 wherein said amine is triethylamine.
9. A method according to Claim 6 wherein said hindered amine base is 2,4,6-trimethylpyridine.

26.5 parts of methylene chloride. The mixture is stirred until all the solid has dissolved. The solution is pale yellow in color. The reaction vessel is cooled to 0-5°C and then 3.8 parts of triethylamine are slowly added. While maintaining the temperature at 0-5°C, 4.8 parts of ethanesulfonyl chloride are added dropwise. The resultant reaction mixture is stirred at 0-5°C for one hour. The reaction mixture is then warmed to room temperature and stirred for an additional hour at room temperature. The vessel is then protected from light and the contents are heated to distill off the methylene chloride. When 13.2 parts of methylene chloride have been collected, 8.5 parts of a xylene mixture are added along with 4.55 parts of 2,4,6-trimethylpyridine which are added dropwise. When the remaining methylene chloride is collected, 8.7 parts of a xylene mixture are added to the reaction vessel. The temperature is maintained at 100°C for five hours after which it is cooled to room temperature. The resultant reaction mixture is very thick with solids and is dark red in color. The mixture is filtered through a sintered glass funnel using an aspirator. Any solids remaining in the reaction vessel are rinsed out with a xylene mixture. The filtrate is dark red in color. The crude product is washed five times with 15.8 parts of methanol. The final filtrate is colorless. The final product, rubrene, is an orange solid. The purified product is dried under vacuum overnight to remove any traces of methanol. 3.7 Parts of rubrene are recovered resulting in a yield of 37%.

Examples 3-5

Following the procedure of Example 1, except as indicated, various alcohols are reacted with various halides to produce substituted naphthacenes. All substituent designations are as set forth above. The results are set forth in Table I, below.

Table I

Ex. No.	Alcohol	Halide		Naphthacene
	R	R ¹	X	R
3	hydrogen	methane	chloride	hydrogen
4	p-chlorophenyl	methane	bromide	p-chloro-phenyl
5	p-methoxyphenyl	ethane	chloride	p-methoxy-phenyl

Claims

1. A method for the preparation of a naphthacene which comprises 1) reacting a solvent solution of a 1,3-diphenylpropargyl alcohol, in the presence of an acid scavenger, with an alkanesulfonyl halide at a temperature of from -30°C to 30°C for from 15 minutes to 3 hours, 2) heating the resultant reaction product to a temperature of from 70°C to reflux from 2 to 8 hours, in an oxygen-free atmosphere, in the absence of light and in the presence of a hindered amine base and 3) recovering the resultant naphthacene.
2. A method according to Claim 1 wherein said acid scavenger is an amine.
3. A method according to Claim 2 wherein said amine is triethylamine.
4. A method according to Claim 1 wherein said hindered amine base is 2,4,6-trimethylpyridine.
5. A method according to Claim 2 wherein said hindered amine base is 2,4,6-trimethylpyridine.
6. A method according to Claim 1 wherein the said solvent in step 1) is methylene chloride and the solvent in step 2) is a xylene mixture.
7. A method according to Claim 6 wherein said acid scavenger is an amine.
8. A method according to Claim 7 wherein said amine is triethylamine.
9. A method according to Claim 6 wherein said hindered amine base is 2,4,6-trimethylpyridine.



10. A method according to Claim 7 wherein said hindered amine base is 2,4,6-trimethylpyridine.
11. A method according to Claim 8 wherein said hindered amine base is 2,4,6-trimethylpyridine.
12. A method according to Claim 1 wherein said oxygen-free atmosphere is provided by nitrogen gas.
13. A method according to Claim 1 wherein said alcohol is 1,1,3-triphenylpropargyl alcohol.
14. A method according to Claim 1 wherein said alkanesulfonyl halide is methanesulfonyl chloride.
15. A method according to Claim 1 wherein said alcohol is 1,1,3-triphenylpropargyl alcohol and said alkanesulfonyl halide is methanesulfonyl chloride.
16. A method according to Claim 15 wherein said acid scavenger is an amine.
17. A method according to Claim 16 wherein said amine is triethylamine.
18. A method according to Claim 15 wherein said hindered amine base is 2,4,6-trimethylpyridine.
19. A method according to Claim 15 wherein said solvent in step 1) is methylene chloride and the solvent in step 2) is a xylene mixture.

15 Revendications

1. Procédé pour la préparation d'un naphtacène qui consiste à 1) faire réagir une solution dans un solvant d'un alcool 1,3-diphénylpropargylique, en présence d'un accepteur d'acide, avec un halogénure d'alcane-sulfonyle à une température de -30°C à 30°C pendant 15 minutes à 3 heures, 2) chauffer le produit réactionnel résultant à une température de 70°C à la température de reflux pendant 2 à 8 heures, dans une atmosphère exempte d'oxygène, en l'absence de lumière et en présence d'une base aminée comportant un empêchement stérique et 3) isoler le naphtacène résultant.
2. Procédé selon la revendication 1, dans lequel ledit accepteur d'acide est une amine.
3. Procédé selon la revendication 2, dans lequel ladite amine est la triéthylamine.
4. Procédé selon la revendication 1, dans lequel ladite base aminée comportant un empêchement stérique est la 2,4,6-triméthylpyridine.
5. Procédé selon la revendication 2, dans lequel ladite base aminée comportant un empêchement stérique est la 2,4,6-triméthylpyridine.
6. Procédé selon la revendication 1, dans lequel ledit solvant de l'étape 1) est le chlorure de méthylène et le solvant de l'étape 2) est un mélange de xylènes.
7. Procédé selon la revendication 6, dans lequel ledit accepteur d'acide est une amine.
8. Procédé selon la revendication 7, dans lequel ladite amine est la triéthylamine.
9. Procédé selon la revendication 6, dans lequel ladite base aminée comportant un empêchement stérique est la 2,4,6-triméthylpyridine.
10. Procédé selon la revendication 7, dans lequel ladite base aminée comportant un empêchement stérique est la 2,4,6-triméthylpyridine.
11. Procédé selon la revendication 8, dans lequel ladite base aminée comportant un empêchement stérique est la 2,4,6-triméthylpyridine.
12. Procédé selon la revendication 1, dans lequel ladite atmosphère exempte d'oxygène est constituée par de l'azote gazeux.
13. Procédé selon la revendication 1, dans lequel ledit alcool est l'alcool 1,1,3-triphénylpropargylique.
14. Procédé selon la revendication 1, dans lequel ledit halogénure d'alcane-sulfonyle est le chlorure de méthane-sulfonyle.
15. Procédé selon la revendication 1, dans lequel ledit alcool est l'alcool 1,1,3-triphénylpropargylique et ledit halogénure d'alcane-sulfonyle est le chlorure de méthane-sulfonyle.
16. Procédé selon la revendication 15, dans lequel ledit accepteur d'acide est une amine.
17. Procédé selon la revendication 16, dans lequel ladite amine est la triéthylamine.
18. Procédé selon la revendication 15, dans lequel ladite base aminée comportant un empêchement stérique est la 2,4,6-triméthylpyridine.
19. Procédé selon la revendication 15, dans lequel ledit solvant de l'étape 1) est le chlorure de méthylène et le solvant de l'étape 2) est un mélange de xylènes.

Ansprüche

1. Verfahren zur Herstellung eines Naphthacens, umfassend 1) die Umsetzung einer Lösungsmittel-Lösung eines 1,3-Diphenylpropargylalkohols in Anwesenheit eines Säurefängers mit einem Alkansulfonylhalogenid bei einer Temperatur von -30°C bis 30°C während von 15 Minuten bis 3 Stunden, 2) das Erhitzen des



resultierenden Reaktionsprodukts auf eine Temperatur von 70°C bis zum Rückfluß während 2 bis 8 Stunden in einer sauerstofffreien Atmosphäre in Abwesenheit von Licht und in Gegenwart einer gehinderten Aminbase und 3) die Isolierung des resultierenden Naphthacens.

2. Verfahren gemäß Anspruch 1, wobei der Säurefänger ein Amin ist.
- 5 3. Verfahren gemäß Anspruch 2, wobei das Amin Triethylamin ist.
4. Verfahren gemäß Anspruch 1, wobei die gehinderte Aminbase 2,4,6-Trimethylpyridin ist.
5. Verfahren gemäß Anspruch 2, wobei die gehinderte Aminbase 2,4,6-Trimethylpyridin ist.
6. Verfahren gemäß Anspruch 1, wobei das Lösungsmittel in Stufe 1) Methylenchlorid ist und das Lösungsmittel in Stufe 2) ein Xylogemisch ist.
- 10 7. Verfahren gemäß Anspruch 6, wobei der Säurefänger ein Amin ist.
8. Verfahren gemäß Anspruch 7, wobei das Amin Triethylamin ist.
9. Verfahren gemäß Anspruch 6, wobei die gehinderte Aminbase 2,4,6-Trimethylpyridin ist.
10. Verfahren gemäß Anspruch 7, wobei die gehinderte Aminbase 2,4,6-Trimethylpyridin ist.
11. Verfahren gemäß Anspruch 8, wobei die gehinderte Aminbase 2,4,6-Trimethylpyridin ist.
- 15 12. Verfahren gemäß Anspruch 1, wobei die sauerstofffreie Atmosphäre durch Stickstoffgas geschaffen wird.
13. Verfahren gemäß Anspruch 1, wobei der Alkohol 1,1,3-Triphenylpropargylalkohol ist.
14. Verfahren gemäß Anspruch 1, wobei das Alkansulfonylhalogenid Methylsulfonylchlorid ist.
15. Verfahren gemäß Anspruch 1, wobei der Alkohol 1,1,3-Triphenylpropargylalkohol ist und das Alkan-
- 20 sulfonylhalogenid Methansulfonylchlorid ist.
16. Verfahren nach Anspruch 15, wobei der Säurefänger ein Amin ist.
17. Verfahren gemäß Anspruch 16, wobei das Amin Triethylamin ist.
18. Verfahren gemäß Anspruch 15, wobei die gehinderte Aminbase 2,4,6-Trimethylpyridin ist.
19. Verfahren gemäß Anspruch 15, wobei das Lösungsmittel in Stufe 1) Methylenchlorid ist und das
- 25 Lösungsmittel in Stufe 2) ein Xylogemisch ist.

30

35

40

45

50

55

